PREDICTING SPONTANEITY

Recall:

For a spontaneous reaction: $\mathbf{\Delta H - T\,\Delta S < 0}$
(constant T and P)

- The value of $\mathbf{\Delta H - T\,\Delta S}$ can be used as a criterion for spontaneity:

If:

- $\mathbf{\Delta H - T\,\Delta S < 0}$ **The reaction is spontaneous from left to right** ($\longrightarrow$)
  The reaction is non-spontaneous from right to left ($\longleftarrow$)
- $\mathbf{\Delta H - T\,\Delta S > 0}$ **The reaction is non-spontaneous from left to right** ($\longrightarrow$)
  The reaction is spontaneous from right to left ($\longleftarrow$)
- $\mathbf{\Delta H - T\,\Delta S = 0}$ **The reaction is at equilibrium** ($\rightleftarrows$)

Examples:

1. Consider the reaction by which urea is prepared from NH_3 and CO_2 , at 25 °C

$$2\,NH_3\,(g) + CO_2\,(g) \longrightarrow CO(NH_2)_2\,(aq) + H_2O\,(l) \qquad \mathbf{\Delta H^0 = -119.7\ kJ}$$

Determine if the reaction is spontaneous from left to right as written.
The value of $\mathbf{\Delta H - T\,\Delta S}$ must be determined:

$\Delta H^0 = -119.7$ kJ
$T = 25 + 273 = 298$ K
$\Delta S = ?$

From Table 18.1:

$S^0(NH_3)$ gas = 193 J/mol x K
$S^0\,(CO_2)$ gas = 214 J/mol x K
$S^0\,[CO(NH_2)_2]$ aqueous = 174 J/mol x K
$S^0(H_2O)$ liquid = 70. J/mol x K

$$\begin{array}{lccccccc} & \mathbf{2\,NH_3\,(g)} & + & \mathbf{CO_2\,(g)} & \longrightarrow & \mathbf{CO(NH_2)_2\,(aq)} & + & \mathbf{H_2O\,(l)} \\ \mathbf{S^0} & 2 \text{ x } 193 & & 214 & & 174 & & 70 \end{array}$$

$$\Delta S^0 = \Sigma n\,S^0(\text{products}) - \Sigma n\,S^0(\text{reactants}) = [(174 + 70] - [2 \text{ x } (193) + (214)] = \boxed{\mathbf{-0.356\ kJ/K}}$$

$\mathbf{\Delta H - T\,\Delta S} = (-119.7\ \text{kJ}) - (298\ \text{K})\,(-0.356\ \text{kJ/K}) = \mathbf{-13.6\ kJ}$

- The reaction is spontaneous under standard conditions from left to right, as written.

GIBBS FREE ENERGY

- Willard Gibbs (American Physicist) brought together the **ΔH** (Enthalpy Change) and **ΔS** (Entropy Change) into a single thermodynamic quantity **G**:

$$\boxed{\mathbf{G = \text{Gibbs Free Energy} = H - TS}}$$

- As a reaction proceeds at a given temperature and pressure:

REACTANTS ⟶ PRODUCTS

$\Sigma n\ \Delta H_f$(reactants) ⟶ $\Sigma m\ \Delta H_f$ (products) | $\Delta H = \Sigma n\ \Delta H_f$(products) - $\Sigma m\ \Delta H_f$(reactants)

$\Sigma n\ S$ (reactants) ⟶ $\Sigma m S$ (products) | $\Delta S = \Sigma n S$ (products) - $\Sigma m S$(reactants)

- Result: For a change at constant T and P : $\boxed{\mathbf{\Delta G = \Delta H - T\Delta S}}$

- For any **<u>spontaneous change</u>** that takes place in a system:
  - Free Energy <u>G must be lowered</u> (Gproducts < Greactants)
  - **<u>ΔG must be negative</u>**: $\Delta G = \Sigma n\ \Delta G$ (products) - $\Sigma m\ \Delta G$(reactants) < 0

– **0** +

$\Delta G < 0$	**$\Delta G > 0$**
• Reaction is spontaneous • Product-favored reaction • Forward reaction is favored	• Reaction is non-spontaneous • Reactant-favored reaction • Reverse reaction is favored

<u>Conclusion</u>:

- ΔG gives a composite of the two factors that contribute to spontaneity (ΔH and ΔS)

SPONTANEITY & FREE ENERGY

- Consider the following situations: $\boxed{\Delta G = \Delta H - T\Delta S}$

1. **ΔH is negative and ΔS is positive** $\boxed{\Delta G = (-) - T(+) = \text{negative}}$ **spontaneous**
   (exothermic) (increase in entropy)

2. **ΔH is positive and ΔS is negative** $\boxed{\Delta G = (+) - T(-) = \text{positive}}$ **non-spontaneous**
   (endothermic) (decrease in entropy)

3. **ΔH is positive and ΔS is positive** $\Delta G = (+) - T(+) = \ ?$
   (endothermic) (increase in entropy)

   - The temperature plays the determining role in controlling spontaneity:

     (a) When T is large: $T\Delta S > \Delta H$ $\boxed{\Delta G = (+) - T_{large}(+) = \text{negative}}$ **spontaneous**

     (b) When T is small: $T\Delta S < \Delta H$ $\boxed{\Delta G = (+) - T_{small}(+) = \text{positive}}$ **non-spontaneous**

4. **ΔH is negative and ΔS is negative** $\Delta G = (-) - T(-) = \ ?$
   (exothermic) (decrease in entropy)

   - The temperature plays the determining role in controlling spontaneity:

     (a) When T is large: $T\Delta S > \Delta H$ $\boxed{\Delta G = (-) - T_{large}(-) = \text{positive}}$ **non-spontaneous**

     (b) When T is small: $T\Delta S < \Delta H$ $\boxed{\Delta G = (-) - T_{small}(-) = \text{negative}}$ **spontaneous**

- The effects of the algebraic signs of **ΔH** and **ΔS** and the effect of temperature on spontaneity can be summarized as:

ΔH	ΔS	ΔG = ΔH – TΔS	Outcome
(–)	(+)	negative	Spontaneous at all temp.
(+)	(–)	positive	Non-spontaneous regardless of temp.
(+)	(+)	negative only at high T	Spontaneous only at high temp.
(–)	(–)	negative only at low T	Spontaneous only at low temp.

FREE ENERGY AT STANDARD STATE

- For interpreting thermodynamic data, standard states are chosen.

Standard States:

- Standard states are indicated by a superscript degree sign on the symbol of the quantity:
    - ΔG^0 = standard free-energy change
    - ΔH^0_f = standard enthalpy change = $\Sigma n\, \Delta H^0_f$(products) - $\Sigma m\, \Delta H^0_f$(reactants)
    - ΔS^0 = standard enthropy change = $\Sigma n S^0$ (products) - $\Sigma m S^0$(reactants)

- Standard states are:

Pressure	Concentration	Temperature
1 atm pressure (for pure liquids and solids) 1 atm partial pressure (for gases)	1 M (for solutions	25 °C (298 K)

Examples:

1. Calculate the standard free-energy change (**ΔG^0**) for the following reaction at 25 °C, and determine whether it is spontaneous or not.

$$CH_4(g) \quad + \quad 2\,O_2 \longrightarrow CO_2(g) \quad + \quad 2\,H_2O(g)$$

ΔH^0_f :	− 74.9	2 x 0	− 393.5	(2) x (− 241.8)
S^0 :	186.1	(2) x (205.0)	213.7	(2) x (188.7)

ΔH^0 $= [-395.5 + (2) \times (-241.8)]\ \text{kJ} - [-74.9 + 0]\ \text{kJ} =$ **− 802.2 kJ**

ΔS^0 $= [213.7 + (2) \times (188.7)]\ \text{J/K} - [186.1 + (2) \times (205.0)] =$ **− 5.0 J/K**

ΔG^0 $= \Delta H^0 - T\Delta S^0 = -802.2\ \text{kJ} - (298\ \text{K})\ (-5.0 \times 10^{-3}\ \text{kJ/K}) =$ **– 800.7 kJ** **(spontaneous)**

2. Calculate the standard free-energy change (**ΔG^0**) for the following reaction at 25 °C, and determine whether it is spontaneous or not.

$$N_2\,(g) \quad + \quad O_2\,(g) \longrightarrow 2\,NO\,(g)$$

ΔH^0_f (kJ/mol)	0	0	90.25
S^0 (J/mol.K)	191.5	205.0	210.7

STANDARD FREE ENERGY OF FORMATION (ΔG^0_f)

- ΔG^0_f is the free-energy change that occurs when 1 mol of substance is formed from its elements in their most stable states at 1 atm and 25 °C
- ΔG^0_f has units of kJ/mol of substance
- ΔG^0_f is a constant, with values available in textbooks.

NOTE: Standard free energies of formation of **elements** in their most stable form = **0**

- ΔG^0 can be calculated directly for any reaction by using:

$$\boxed{\Delta G^0 = \Sigma\, n\Delta G^0_f(\text{products}) - \Sigma\, m\Delta G^0_f(\text{products})}$$

Examples:

1. Calculate the standard free energy of the following reaction at 25 °C, using standard free energies of formation given below:

$$Na_2CO_3\,(s) + H^+\,(aq) \longrightarrow 2\,Na^+\,(aq) + HCO_3^-\,(aq)$$

ΔG^0_f : -1048.1 0 $(2) \times (-261.9)$ -587.1

$\Delta G^0_f = [(2) \times (-261.9) + (-587.1)] - [(-1048.1) + 0]\text{ kJ} = \mathbf{-62.8\text{ kJ}}$

3. Calculate the standard free-energy change (ΔG^0) for the reaction shown below, and determine whether it is spontaneous or not. (Use ΔG^0_f values in your textbook).

$$2\,NOCl\,(g) \longrightarrow 2\,NO\,(g) + Cl_2\,(g)$$

ΔG^0 AS A CRITERION FOR SPONTANEITY

$\Delta G < -10$ kJ	**-10 kJ $< \Delta G < +10$ kJ**	**$\Delta G > +10$ kJ**
Large negative number	Small negative or positive number	Large positive number
Reaction is spontaneous	Reaction gives an equilibrium mixture	Forward reaction is non-spontaneous Reverse reaction is spontaneous
Reactants $\longrightarrow$ Products	Reactants $\rightleftharpoons$ Products	Reactants $\longleftarrow$ Products
Reactants transform entirely to products	Significant amount of both reactants and products present	Mostly reactants present

Examples:

1. Which of the following reactions are spontaneous in the direction written? (See table in your textbook for ΔG^0_f values.

(A)

	$C(graphite)$	+	$2\,H_2(g)$	$\longrightarrow$	$CH_4(g)$
ΔG_f^0 :	0		0		– 50.8

ΔG^0 = [(–50.80 – (0)] kJ = **–50.8 kJ** **(spontaneous reaction)**

(B)

	$Ag^+(aq)$	+	$I^-(aq)$	$\longrightarrow$	$AgI(s)$
ΔG_f^0 :	77.1		–51.7		–66.3

ΔG^0 =

2. Consider the reaction of nitrogen, N_2 and oxygen, O_2 to form nitric oxide, NO:

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g)$$

The standard free energy of formation of NO is + 86.60 kJ/mol. Do you expect the reaction to be spontaneous as written?

Recall: Standard free energies of formation of **elements** in their stablest form = **0**

ΔG^0 = 2 (+ 86.60 kJ) = **+ 173.2 kJ** **(non-spontaneous reaction)**

FREE ENERGY and USEFUL WORK

- In a spontaneous reaction:
  - the "free" energy is lowered as reactants change to products,
  - the change in "free" energy is released as free-energy change(**ΔG)**
  - this "**ΔG**" can be harnessed to perform useful work

A spontaneous reaction can be used to obtain useful work

Examples:

1. The combustion of gasoline is used to move a car
2. The reaction in a battery generates electricity that can drive a motor

The free – energy change (ΔG) is the maximum energy available ("free") to do useful work

Maximum useful work = $\boxed{w_{max} = \Delta G}$

- In an **ideal** situation: $\Delta G \xrightarrow[\text{converted into}]{\text{completely}} \text{Useful work}$
- In **real** situations: $\Delta G \xrightarrow[\text{into}]{\text{converted}} \text{Some Useful Work + Some Entropy}$

Conclusions:

1. In theory, all of the free-energy decrease liberated during a spontaneous chemical change can be used to do work (this would be **w_{max})**

2. In practice, less work is obtained and the difference appears as an increase in entropy

Example:

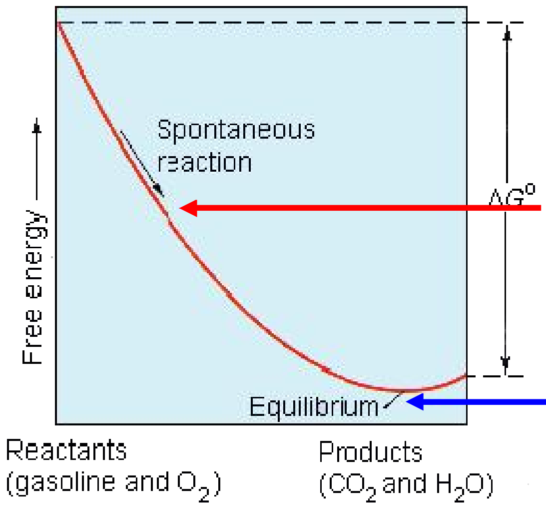
- Living systems are able to convert only about 40% of the free energy available in the oxidation of glucose to other forms of stored chemical energy (for example , ATP).

- The rest (60%) appears as heat, which ensures the body's effective temperature control system.

FREE-ENERGY CHANGE DURING A SPONTANEOUS REACTION

(combustion of gasoline)

$$\text{Gasoline} + O_2 \longrightarrow CO_2(g) + H_2O(g)$$



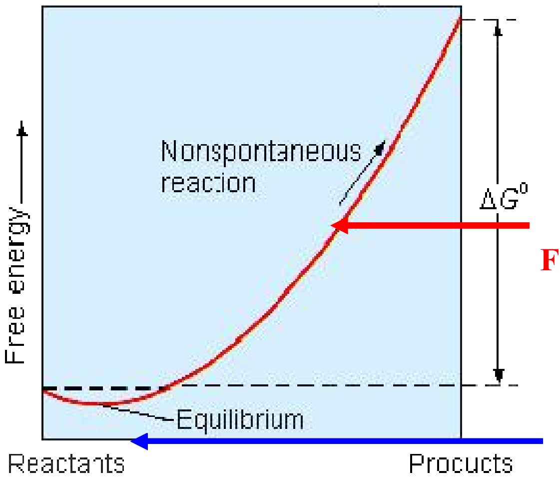
Free energy decreases as the reaction proceeds (ΔG < 0)

At equilibrium, free energy is at a minimum (equilibrium mixture is mostly products)

FREE-ENERGY CHANGE DURING A NON-SPONTANEOUS REACTION

(synthesis of NO from elements)

$$N_2(g) + O_2(g) \longrightarrow 2\ NO(g)$$



Free energy increases as the reaction proceeds (ΔG > 0)

There is a small decrease in free energy as the system goes to equilibrium (some reaction occurs to give the equilibrium mixture which consists mostly of reactants)

$$N_2(g) + O_2(g) \longrightarrow NO(g)$$

ΔG^0 & THE EQUILIBRIUM CONSTANT

- **ΔG** determines the maximum amount of energy that is available to perform useful work as a system passes from one state to another (**$\Delta G = G_{products} - G_{reactants}$**)

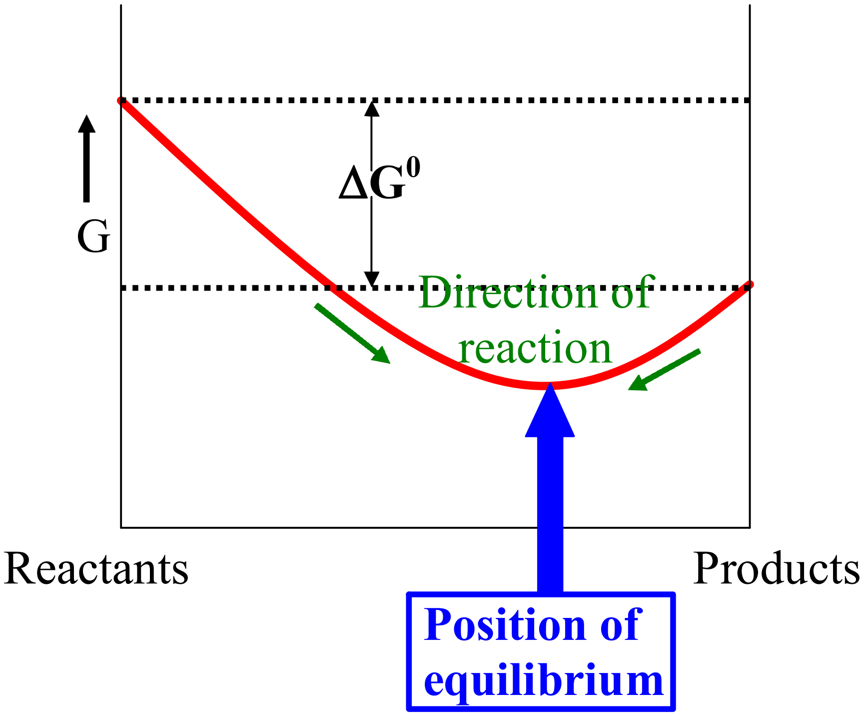
- As a reaction proceeds:
  - the system's capacity to perform useful work decreases (ΔG diminishes),
  - the system eventually reaches equilibrium and $\Delta G \approx 0$ (Free Energy ceases to change)

- The value of **ΔG** determines where the system stands with respect to equilibrium:

When $\Delta G < 0$	**When $\Delta G = 0$**	**When $\Delta G > 0$**
The reaction is spontaneous and proceeds in the forward direction towards equilibrium (G decreases)	The system is in a state of dynamic equilibrium	The reaction is not spontaneous in the forward direction. The reaction is spontaneous in the reverse direction.

Qualitative Relationship between ΔG^0 and the Position of Equilibrium

- The direction in which a reaction proceeds toward equilibrium is determined by where the system lies with respect to the free-energy minimum.



NOTE:

- The reaction proceeds spontaneously only in a direction that gives rise to a decrease in free energy (ΔG is negative)

RELATIONSHIP BETWEEN ΔG⁰ AND EQUILIBRIUM CONSTANT

$$\Delta G = \Delta G^0 + RT \ln Q$$

Q = Thermodynamic Reaction Quotient

- for reactions involving gases Q is obtained from partial pressures.
- for reactions in solutions, Q is obtained from molar concentrations

R = Gas Law Constant in units of energy = 8.314 J/mol K

ΔG^0 = Standard Free-Energy Change

ΔG = Free-Energy Change when Reactants in nonstandard states are changed to products in non-standard states

At equilibrium:

1. The free energy ceases to change: ⇨ **$\Delta G = 0$**
2. The Thermodynamic Reaction Quotient, Q becomes equal to the Thermodynamic Equilibrium Constant (K): ⇨ **$Q = K$**

$\Delta G = \Delta G^0 + RT \ln Q$ becomes: $0 = \Delta G^0 + RT \ln K$

By rearrangement: $\boxed{\Delta G^0 = -RT \ln K}$ **or** $\boxed{\Delta G^0 = -2.303\, RT \log K}$

Basic Equations relating the standard free-energy change to the equilibrium constant.

- Natural logarithms (ln) and logarithms to the base 10 (log) are related by: $\ln x = 2.303 \log x$

$\boxed{\Delta G^0 = -2.303\, RT \log K}$ ⇢ **Thermodynamic Equilibrium Constant**

- The equilibrium Constant in which:
  - the concentration of **gases** are expressed in **partial pressures** in atmospheres.
  - the concentration of **solutes** are expressed in **molarities**
- It follows that:
  1. For reactions involving only gases: **$K = K_p$**
  2. For reactions involving only solutes in liquid solutions: **$K = K_c$**
  3. For net ionic equations: **$K = K_{sp}$**

RELATIONSHIP OF ΔG^0, K, AND SPONTANEITY

$$\boxed{\Delta G^0 = -2.303\ RT \log K}$$

When K > 1	**When K ≈ 1**	**When K <1**
Reactants transform almost entirely to products	Significant amounts of both reactants and products are present	Mostly reactants present
Reactants $\longrightarrow$ Products	Reactants $\rightleftarrows$ Products	Reactants $\longleftarrow$ Products
$\log K > 0$	**$\log K \approx 0$**	**$\log K < 0$**
$\Delta G^0 < 0$	**$\Delta G^0 = \pm 10$ kJ** **$K = (0.018 – 57)$**	**$\Delta G^0 > 0$**
Reaction is **spontaneous**	Reaction gives an **equilibrium mixture**	**Forward** reaction is **non-spontaneous** **Reverse** reaction is **spontaneous**

Examples:

1. Use the standard free energies of formation given to determine the equilibrium constant (K) for the following reaction at 25 °C:

	$N_2\,(g)$	+	$3\,H_2\,(g)$	$\rightarrow$	$2\,NH_3\,(g)$
ΔG^0_f (kJ/mol)	0		0		–16.66

$$\Delta G^0 = [\,2 \times \Delta G^0_f(NH_3)] - [\,\Delta G^0_f(N_2) + 3 \times \Delta G^0_f(H_2)] = 2 \times (-16.66) - 0 = -33.32 \text{ kJ}$$

$$\Delta G^0 = -RT \ln K \qquad \ln K = \frac{-\Delta G^0}{RT} \qquad K = e^{\Delta G^0/RT}$$

$$\frac{-\Delta G^0}{RT} = \frac{-(-33,320 \text{ J})}{(8.314 \text{ J/K})(298 \text{ K})} = 13.45 \qquad K = e^{13.45} = 6.9 \times 10^5$$

2. Use the standard free energies in your text to calculate ΔG^0 and K for the following reaction at 25 °C:

$$2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(g)$$

CHANGE OF FREE ENERGY WITH TEMPERATURE

- How can ΔG^0 be found for temperatures other than standard temperatures (25 °C)?
- An approximate method used to calculate ΔG^0_T is based on the assumption that both ΔH^0 and ΔS^0 are constant with respect to temperature (only approximately true)
- Then: $\boxed{\Delta G^0_T = \Delta H^0 - T\Delta S^0}$ (a convenient approximation for ΔG^0_T)

NOTE: **ΔG^0_T is strongly temperature dependent**

ΔG^0_T = Change in free Energy for a substance:
- at 1 atm of pressure (standard pressure) and
- at the specified temperature, T (nonstandard temperature)

SPONTANEITY $\xrightarrow{\text{depends on the value of}}$ ΔG^0_T $\xrightarrow{\text{determined by}}$ **TEMPERATURE**

- It follows that **SPONTANEITY IS TEMPERATURE DEPENDENT**!

Meaning:
- Some chemical changes may be non-spontaneous at one temperature but spontaneous at another temperature.

Effect of Temperature on the Spontaneity of Reactions

$\boxed{\Delta G^0_T = \Delta H^0 - T\Delta S^0}$ $\boxed{\textbf{For a Spontaneous Reaction: } \Delta G^0_T < 0}$

ΔH^0	ΔS^0	**Temperature**	ΔG^0	**Spontaneity**
(–)	(+)	no effect	Negative regardless of temp.	Spontaneous at any temp.
(+)	(–)	no effect	Positive regardless of temp.	Non-spontaneous at any temp.
(–)	(–)	Low	Negative	Spontaneous at low temp.
		High	Positive	Non-spontaneous at high temp.
(+)	(+)	Low	Positive	Non-spontaneous at low temp.
		High	Negative	Spontaneous at high temp.

Examples:

1. When glucose ferments, it produces ethyl alcohol and carbon dioxide. The reaction is exothermic. Under what temperature conditions is this reaction spontaneous?

$$\underset{\text{glucose}}{C_6H_{12}O_6\,(s)} \longrightarrow \underset{\text{ethyl alcohol}}{2\,C_2H_5OH\,(l)} + 2\,CO_2(g) \qquad \boxed{\Delta H^0 < 0}$$

$$\left.\begin{array}{ccc} \text{1 molecule} & \text{breaks} & \text{2 molecules of liquid} \\ \text{of} & \longrightarrow & \text{and} \\ \text{solid} & \text{into} & \text{2 molecules of gas} \end{array}\right\} \Rightarrow \boxed{\Delta S^0 > 0}$$

$$\boxed{\Delta G^0_T = \Delta H^0 - T\Delta S^0} = \boxed{\textbf{(Negative Number)}} - \textbf{[(Temperature) x} \boxed{\textbf{(Positive Number)]}}$$

$$\boxed{\Delta G^0_T = \Delta H^0 - T\Delta S^0} = \boxed{(-) \quad - \quad [\quad (+) \quad]}$$

NOTE: T is absolute temperature in K cannot be negative

- **ΔG^0_T is negative (regardless of temperature)**
- **Reaction is spontaneous at any temperature**

2. Sodium Carbonate, Na_2CO_3, can be prepared by heating sodium hydrogen carbonate, $NaHCO_3$. Estimate the temperature at which $NaHCO_3$ decomposes to products at 1 atm.

$$2\,NaHCO_3\,(s) \longrightarrow Na_2CO_3 + H_2O\,(g) + CO_2\,(g)$$

- First calculate the ΔH^0 **and** ΔS^0, using the given ΔH_f^0 and S^0 values:

	$2\,NaHCO_3\,(s)$ $\longrightarrow$	Na_2CO_3 +	$H_2O\,(g)$ +	$CO_2\,(g)$
ΔH_f^0 :	2 x (–947.7)	–1130.8	–241.826	–393.5
ΔS^0 :	2 x 102	139	188.72	213.7

$\Delta H^0 = [(-1130.8) + (-241.826) + (-393.5)] - [\,(2) \times (-947.7)] = \mathbf{129.\underline{2}74\ kJ}$

$\Delta S^0 = [(139) + (188.72) + (213.7)] - [\,92) \times (102)] = 33\underline{7}.4\ J/K = \mathbf{0.33\underline{7}4\ kJ/K}$

- Substitute these values into $\Delta G^0 = \Delta H^0 - T\Delta S^0$; Let $\Delta G^0 = 0$

$$\Delta H^0 - T\Delta S^0 = 0 \qquad T = \frac{\Delta H^0}{\Delta S^0} = \frac{129.\underline{2}74\ kJ}{0.33\underline{7}4\ kJ/K} = \mathbf{383\ K\ \ (110\,°C)} \qquad \mathbf{[T \geq 383\ K\ (110\,°C)]}$$

The temperature at which **$NaHCO_3$** decomposes to products at 1 atm. should be at least = **383 K (110 °C)**

3. Oxygen was first prepared by heating mercury(II) oxide, HgO. Estimate the temperature at which HgO decomposes to O_2 at 1 atm.

$$\mathbf{2\,HgO\,(s) \longrightarrow 2\,Hg\,(g) + O_2(g)}$$

- First calculate the ΔH^0 **and** ΔS^0, using the given ΔH_f^0 and S^0 values:

	2 HgO(s)	**2 Hg (g)**	**+**	**O_2 (g)**
ΔH_f^0 :	–90.8	61.3		0
ΔS^0 :	70.3	174.9		205.0

$\Delta H^0 =$

$\Delta S^0 =$

- Substitute these values into $\Delta G^0 = \Delta H^0 - T\Delta S^0$; Let $\Delta G^0 = 0$

$$\Delta H^0 - T\Delta S^0 = 0 \qquad T = \frac{\Delta H^0}{\Delta S^0} =$$